OPIC | CIPO

Ottawa Hull K1A 0C9

(21) (A1) 2,157,806
(22) 1995/09/08
(43) 1997/03/09

(51) Int.Cl.[6] C09J 123/26

(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

# (54) Polypropylene-Based Hot-Melt Adhesive

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(57) 21 Claims

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Cover Page Not Yet Available

## ABSTRACT OF THE DISCLOSURE

An adhesive composition comprising a melt blend of:

(a) 40-95% by weight of polypropylene; and

(b) 5-60% by weight of at least one copolymer of ethylene and at least one alkyl acrylates, in which the alkyl group has 1-8 carbon atoms, said blend having been grafted with at least one ethylenically-unsaturated carboxylic acid or anhydride, or derivative thereof. The adhesive composition has a melt viscosity suitable that is thermally stable for at least eight hours and is suitable for use as a hot melt adhesive.

# POLYPROPYLENE-BASED HOT-MELT ADHESIVE

The present invention relates to improvements in polypropylene-based hot-melt adhesive compositions which are capable of bonding a polypropylene substrate to another substrate. In particular, the present invention relates to a polypropylene-based hot-melt adhesive composition that exhibits improvements in thermal stability and also is capable of being subjected to recycling processes for polypropylene. As used herein, "thermal stability" is measured in a Brookfield viscometer at 220°C at 5 rpm using spindle #29, and compositions are considered to exhibit thermal stability if the increase in viscosity is less than 25% after eight hours.

Structures may be bonded together using a variety of adhesives. Adhesives capable of bonding polypropylene substrates include compositions formed from polypropylene and ethylene/vinyl acetate copolymers, in which the individual polymers or the blend of polymers has been grafted with maleic anhydride. While such an adhesive composition exhibits good bond strength, it has been found that it exhibits acceptable thermal stability at 220°C for only about four-six hours, as exemplified hereinafter, after which period of time the adhesive composition is not capable of being processed in apparatus for hot-melt adhesives nor are adhesive properties maintained. While the adhesive properties may be acceptable in some end uses, the limited thermal stability imposes limitations on the variety of end uses for which the adhesive composition may be used. Improvement in thermal stability, to greater than eight hours at 220°C, is required for practical application of the adhesive composition in many hot-melt adhesive end uses.

The grafting of ethylenically-unsaturated carboxylic acids or anhydrides onto polyolefins is

described in U.S. Patent 4 612 155 of R.A. Zelonka and C.S. Wong, which issued September 16, 1986.

U.S. Patent 5 241 014 of H. Kehr et al. discloses the production of largely amorphous polyalpha-olefins with a narrow molecular weight distribution by subjecting largely amorphous polyalpha-olefins containing 3-75 weight percent of $C_4$-$C_{10}$ alpha-olefin, 25-95 weight percent of propylene and 0-20 weight percent ethylene monomer units to a shearing force at a temperature above the softening point of the polymer in the presence of a radical donor. Grafting reactions may be conducted at the same time. The polymers are stated to be useful as hot-melt adhesives.

An adhesive composition has been found that is capable of bonding a polypropylene substrate to another substrate, and of being recycled with polypropylene, and which exhibits a thermal stability at 220°C of greater than eight hours.

Accordingly the present invention provides an adhesive composition comprising a blend of:

(a) 40-95% by weight of polypropylene; and

(b) 5-60% by weight of at least one copolymer of ethylene and at least one alkyl acrylate having 3-50 mol % of alkyl acrylate, in which the alkyl group has 1-8 carbon atoms;

said blend having been grafted with at least 0.1% of at least one ethylenically-unsaturated carboxylic acid or anhydride or derivative thereof;

said adhesive composition having a thermal stability, as defined, of greater than eight hours at 220°C.

In a preferred embodiment of the composition, the blend has been grafted with 0.5-2.0% by weight of the ethylenically unsaturated carboxylic acid or anhydride, or derivative thereof. In another embodiment, the blend has a melt viscosity in the range of 5000-75000 cps at 220°C.

Furthermore, the present invention provides a process for the bonding of a first substrate to a second substrate, in which at least one of the substrates is polypropylene, comprising coating the first substrate with a molten composition of a blend of:

(a) 40-95% by weight of polypropylene; and

(b) 5-60% by weight of at least one copolymer of ethylene and at least one alkyl acrylate having 3-50 mol % of alkyl acrylate, in which the alkyl group has 1-8 carbon atoms;

said blend having been grafted with at least 0.1% of at least one ethylenically-unsaturated carboxylic acid or anhydride or derivative thereof;

said adhesive composition having a thermal stability, as defined, of greater than eight hours at 220°C; and

contacting the second substrate with the molten adhesive and cooling the resultant bonded structure.

In preferred embodiments of the processes of the present invention, at least one and preferably both of the substrates is formed from polypropylene, including mineral-filled, foamed or woven polypropylene, and polypropylene film, including oriented film. The film may be surface modified by corona-discharge treatment or electrostatic treatment.

The polymer of component (a) is polypropylene. As used herein, the expression "polypropylene" refers to homopolymers of propylene, to impact or so-called block copolymers of propylene with ethylene in which the ethylene content is less than about 25% by weight and to random copolymers of propylene with ethylene in which the ethylene content is less than about 8% by weight.

The copolymer of component (b) is a copolymer of ethylene and at least one alkyl acrylate, in which the alkyl group is 1-8 carbon atoms. In preferred embodiments, the alkyl group is methyl. The copolymer

has 3-50 mol % of alkyl acrylate monomer, with the balance being ethylene.

The monomer used in the grafting of the copolymers is at least one monomer selected from ethylenically unsaturated carboxylic acids and ethylenically unsaturated carboxylic acid anhydrides, including, derivatives of such acids or anhydrides, and mixtures thereof. Examples of the acids and anhydrides, which may be mono-, di- or polycarboxylic acids, are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, itaconic anhydride, maleic anhydride, and substituted maleic anhydride, e.g. dimethyl maleic anhydride or citraconic anhydride, nadic anhydride, nadic methyl anhydride, and tetrahydrophthalic anhydride, maleic anhydride being particularly preferred. Examples of the derivatives of the unsaturated acids are salts, amides, imides and esters e.g. mono- and disodium maleate, acrylamide, maleimide, glycidyl methacrylate, monoethyl maleate and dimethyl fumarate. The present invention will be particularly described herein with reference to maleic anhydride as the grafting monomer.

The blend that is grafted is formed from 40-95% by weight polypropylene, especially 50-95% by weight polypropylene, and 5-60% by weight of the ethylene/alkyl acrylate copolymer, especially 5-50% by weight thereof.

The adhesive composition of the present invention has a melt viscosity suitable for use as a hot-melt adhesive, especially a melt viscosity in the range of 5,000-75,000 cps at 220°C, and particularly 10,000-50,000 cps at 220°C. Moreover, adhesive compositions of the present invention exhibit a stability at 220°C of greater than eight hours, as discussed herein.

The grafted monomer content of the blend is preferably at least 0.1% by weight, and especially 0.1-5.0% by weight, more especially 0.1-2.0% by weight. In embodiments, the grafted monomer content is at least

0.5% by weight and especially in the range of 0.5-2.0% by weight.

It is also known to use blends of grafted polymer compositions with ungrafted polyolefins in order to achieve a desired level of graft in a composition, and such blending in of ungrafted components may be used herein. Such ungrafted polyolefins are polypropylene and/or ethylene/alkyl acrylate copolymer as defined herein.

The polymers that form the adhesive composition are dry blended prior to being fed to apparatus or are fed separately to such apparatus for grafting of the ethylenically-unsaturated carboxylic acid or anhydride or derivative thereof or are fed separately to such apparatus. Consequently, the adhesive compositions may be referred to as co-grafted compositions. Techniques for the grafting of such monomers onto the copolymers are known e.g. as described in U.S. Patent 4 612 155 of R.A. Zelonka and C.S. Wong, which issued September 16, 1986, and in published European patent application No. 0 369 604 of D.J. Mitchell, published May 23, 1990.

The adhesive is applied directly onto a substrate i.e. while the adhesive is still in a molten condition. Apparatus suitable for the blending or mixing of the adhesive and for application of a hot melt adhesive to a substrate are known. The adhesive is applied to a first substrate in a molten condition and then the second substrate is applied over the adhesive while the adhesive is still in a molten condition. Contact of the adhesive while molten with both substrates is important in order to achieve a good bond.

While a variety of substrates may be bonded together using the adhesive composition described herein, in preferred embodiments at least one and especially both substrates are formed from polypropylene. Examples of particularly preferred substrates are mineral-filled polypropylene e.g. mica-filled polypropylene, foamed

polypropylene, and woven polypropylene including fabrics, woven tapes and the like. The substrate may be polypropylene film, especially oriented polypropylene film, including corona discharge-treated and electrostatic-treated films.

The adhesive composition and process of the invention may be used in the bonding of substrates, especially polypropylene. In the latter instance, use of the adhesive composition permits the opportunity of recycling the bonded substrates, as the polymeric components are based upon polypropylene and the recycled components would not significantly degrade the physical properties of polypropylene when blended therein as a minor component. Such polypropylene of the substrate would have a melt index (or melt flow index) and other characteristics of polypropylenes used in the forming of articles, which would depend in part on the particular end-use.

The adhesive forms strong bonds with polypropylene, as illustrated below, but may be used with other substrates. The adhesive may be used in a wide variety of industrial applications, including for example in the automotive industry, and in the manufacture of furniture, appliances and small electronic equipment.

The present invention is illustrated by the following examples. Melt Index was measured by the procedure of ASTM D-1238 (190°C/2.16) unless specified to the contrary.

EXAMPLE I

An adhesive composition of the present invention was formed from a mixture of 82 parts by weight of a copolymer of polypropylene having 4% by weight of ethylene as comonomer and a melt flow index (procedure of ASTM D-1238 (230°C/2.16)) of 5 dg/min with 18 parts by weight of an ethylene/methyl acrylate copolymer containing 28% by weight of methyl acrylate comonomer and having a melt index of 175 dg/min. The resultant mixture

was grafted with 1.0% by weight of maleic anhydride using a melt grafting process and a free radical initiator, to give a graft level of 0.75% by weight in the grafted polymer. The melt index of the grafted copolymer obtained was 220 dg/min.

As a comparison, the adhesive composition was formed from a mixture of 80 parts by weight of a copolymer of polypropylene with 4% by weight of ethylene as comonomer and having a melt flow index of 5 dg/min with 20 parts by weight of an ethylene/vinyl acetate copolymer containing 28% by weight of vinyl acetate comonomer and having a melt index of 800 dg/min. The mixture was grafted with 1.8% by weight of maleic anhydride using a melt grafting process and a free radical initiator, to give a graft level believed to be about 0.65% by weight in the grafted polymer. The melt index of the grafted copolymer obtained was 260 dg/min.

Each of the adhesive compositions were placed in a Brookfield viscometer at a temperature of 220°C. The viscometer was operated at 5 rpm using spindle #29. The viscosity of the adhesive composition was monitored over a period of time. The results obtained are shown in Table I.

Table I

| Time (minutes) | Viscosity* (cps) PP/EVA | PP/EMA |
|---|---|---|
| 15 | 32,600 | 25,800 |
| 80 | 28,200 | 21,000 |
| 120 | 27,200 | 20,800 |
| 240 | 26,400 | 20,800 |
| 360 | 31,600 | 20,800 |
| 420 | 50,000 | 20,800 |
| 480 | 88,000 | 20,800 |
| 1460 | - | 21,000 |

PP/EVA = polypropylene/ethylene-vinyl acetate copolymer composition

PP/EMA = polypropylene/ethylene-methyl acrylate copolymer composition

The results show that the adhesive composition formed from the polypropylene and ethylene/methylacrylate blend had a stable thermal viscosity over a period of 1,460 minutes (more than 24 hours).

In contrast, the comparative adhesive composition formed from the polypropylene and ethylene/vinyl acetate copolymer showed a stable thermal viscosity for only about 4 hours, after which there was a steady and then a rapid increase in viscosity. For this composition, the test was terminated after eight hours due to equipment torque limitations resulting from the rapid increase in viscosity.

EXAMPLE II

The adhesive composition and comparative composition of Example I were subjected to peel tests. Each of the compositions were subjected to a temperature of 220°C in hot-melt equipment for a period of time. Adhesive test samples were then prepared using a 35% mica-filled homopolymer polypropylene rigid plaque as one substrate and a polyester fabric as the second substrate. The adhesive had a thickness of approximately 75 mil. The substrates were bonded at a temperature of 220°C using a weight of 1,000 g and a pressing time of 30 seconds. The resultant bonded samples, having a bonded area which measured 2.5 x 7.6 cm, were then peeled apart at an angle of 180°, using an Instron with a cross head speed of 25 cm/min. The peel tests were conducted at room temperature (23°C).

The results obtained are shown in Table II.

Table II - 180° Peel Tests

| Exposure Time (hours) | Adhesion* (pli) PP/EVA | PP/EMA |
|---|---|---|
| 1 | 27 | 18 |
| 6 | 18 | 18 |
| 24 | n/a | 28 |

* measured in lbs/inch

In the 180° peel test of the adhesive after an exposure time of 24 hours, the failure was a substrate failure.

Table II shows that the adhesion results were the same for both adhesive compositions after period of six hours. However, after exposure to 220°C for a period of seven hours, it was not possible to form an adhesive composition from the ethylene/vinyl acetate composition due to the amount of gel that had been formed and the inability of the hot-melt dispensing equipment to feed the formulation. In contrast, the composition of the present invention could be used to prepare samples, even after 24 hours of exposure to 220°C.

The results show the substantial improvement in adhesive stability and adhesive application results obtained using the adhesive composition of the present invention.

CLAIMS:

1. An adhesive composition comprising a blend of:

(a) 40-95% by weight of polypropylene; and

(b) 5-60% by weight of at least one copolymer of ethylene and at least one alkyl acrylate having 3-50 mol % of alkyl acrylate, in which the alkyl group has 1-8 carbon atoms;

said blend having been grafted with at least 0.1% by weight of at least one ethylenically-unsaturated carboxylic acid or anhydride or derivative thereof;

said adhesive composition having a thermal stability, as defined, of greater than eight hours at 220°C.

2. The adhesive composition of Claim 1 in which the alkyl group is methyl.

3. The adhesive composition of Claim 1 or Claim 2 in which the blend has been grafted with 0.1-5.0% by weight of the ethylenically unsaturated carboxylic acid or anhydride, or derivative thereof.

4. The adhesive composition of Claim 3 in which the blend has been grafted with at least 0.5% by weight of said at least one ethylenically unsaturated carboxylic acid or anhydride, or derivative thereof.

5. The adhesive composition of Claim 3 in which the blend has been grafted with 0.5-2.0% by weight of the ethylenically unsaturated carboxylic acid or anhydride, or derivative thereof.

6. The adhesive composition of any one of Claims 1-5 in which the adhesive composition contains un-rafted ethylene/methyl acrylate copolymer.

7. The adhesive composition of any one of Claims 1-6 in which the adhesive composition contains un-rafted polypropylene.

8. The adhesive composition of any one of Claims 1-7 in which the melt viscosity is 5000-75000 cps at 220°C.

9. The adhesive composition of Claim 8 in which the melt viscosity is 10000-50000 cps at 220°C.

10. The adhesive composition of any one of Claims 1-9 in which the blend has 50-95% by weight of polypropylene and 5-50% by weight of the ethylene/alkyl acrylate copolymer.

11. A process for the bonding of a first substrate to a second substrate, in which at least one of the substrates is polypropylene, comprising coating the first substrate with a molten composition of a blend of:

(a) 40-95% by weight of polypropylene; and

(b) 5-60% by weight of at least one copolymer of ethylene and at least one alkyl acrylate having 3-50 mol % of alkyl acrylate, in which the alkyl group has 1-8 carbon atoms;

said blend having been grafted with at least 0.1% by weight of at least one ethylenically-unsaturated carboxylic acid or anhydride or derivative thereof;

said adhesive composition having a thermal stability, as defined, of greater than eight hours at 220°C; and

contacting the second substrate with the molten adhesive and cooling the resultant bonded structure.

12. The process of Claim 11 in which the alkyl group is methyl.

13. The process of Claim 11 or Claim 12 in which both of the substrates are formed from polypropylene.

14. The process of any one of Claims 11-13 in which the polypropylene substrate is mineral-filled, foamed or woven polypropylene or film.

15. The process of any one of Claims 11-14 in which the blend has been grafted with at least 0.5% by weight of said at least one ethylenically unsaturated carboxylic acid or anhydride, or derivative thereof.

16. The process of Claim 15 in which the blend has been grafted with 0.5-2.0% by weight of the ethylenically unsaturated carboxylic acid or anhydride, or derivative thereof.

17. The process of any one of Claims 11-16 in which the adhesive composition contains un-grafted ethylene/methyl acrylate copolymer.

18. The process of any one of Claims 11-17 in which the adhesive composition contains un-grafted polypropylene.

19. The process of any one of Claims 11-18 in which the melt viscosity is 5 000-75 000 cps at 220°C.

20. The process of Claim 19 in which the melt viscosity is 10 000-50 000 cps at 220°C.

21. The process of any one of Claims 11-20 in which the blend has 50-95% by weight of polypropylene and 5-50% by weight of the ethylene/alkyl acrylate copolymer.